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Synthesis and Characterization of PolyEthylene Glycol-g-Arginine and its Corrosion - Inhibition Behaviour on Mild Steel

S. Sheeba joy bell, R. Geethanjali , S. Subhashini*

Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, TN, India.

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Abstract

Aqueous chemical process is an environment-friendly efficient technique used to prepare conducting polymers. It is widely preferred because of its simplicity and it can be used as one step method. A polymer was prepared by grafting amino acid Arginine (A) on polyethylene glycol (PEG) in different ratios. The structure of the polymer composite was characterized using FT-IR, X-Ray diffraction and UV absorption spectroscopy. The water soluble polymers gained attraction of the researchers in the corrosion inhibition because of the available lone pair of electrons. In the present study, water-soluble PEG-g-A is explored for its inhibitive action on mild steel corrosion in acid media. The polymer was evaluated using polarization studies and electrochemical impedance spectroscopy. The evaluation revealed that the polymer as an effective mixed-type inhibitor in the HCl and H_2SO_4 media. The charge transfer resistance and double layer capacitance values confirmed the adsorption of the polymer on the metal surface. The open circuit potential study proved the formation of polymer film on the metal surface and the stability of the formed film.

***Keywords**: Arginine; Corrosion inhibition; Mild steel; Polyethylene Glycol.*

1. INTRODUCTION

The significance of corrosion problems and its control is of worldwide interest for centuries. In order to remove the rust on the surface of the metallic materials, acid pickling is usually carried out. During the process metal loss is eliminated by the use of inhibitors. Organic compounds are proven inhibitors, but due to the increasing environmental concerns their use has been restricted. This lead to the search for new inhibitors, which are environmentally safe and have better corrosion-restricting ability similar to organic compounds. These criteria are well met by polymers like polyvinyl alcohol, polyethylene glycol, polyvinyl pyrrolidone, pectin, carboxymethyl cellulose etc . This paper is a report of synthesis of such an environmentally benign polymer using polyethylene glycol and amino acid arginine. Polyethylene glycol is chosen because it is non-toxic and has flexible chains with C, O and H. But PEG has been reported with corrosion inhibition efficiency of 60% by Umoren *et al.* (2008). We have improved the inhibition efficiency of polyethylene glycol by grafting it with amino acid arginine (PEG-g-A) in smaller quantities and investigated the improved corrosion inhibition performance by electrochemical methods.

***S.Subhashini**
E-mail: subhash_sethu@gmail.com*

2. EXPERIMENTAL

2.1 Synthesis of PEG-g-A

The graft polymerization of polyethylene Glycol with amino acid Arginine has been carried out by oxidative polymerization using ammonium peroxodisulphate as oxidant in oxalic acid medium. During polymerization polyethylene Glycol and amino acid were mixed in different ratios viz 1:1 (PEG-g-A1), 1:2 (PEG-g-A2), 2:1 (PEG-g-A3) in distilled water and cooled to 0°C- 4°C. 0.5M ammonium persulphate, prepared in 0.5M oxalic acid was added drop wise to the reaction mixture with constant stirring for 2-3 hrs. After addition the solution was kept in refrigerator for 24 hrs. Then the polymer solution was neutralized with ammonium hydroxide. The polymer was precipitated with acetone. The polymer was then dried under dynamic vacuum.

2.1.1 Solubility

The solubility of the polymers was tested in different polar and nonpolar solvents like water, ethanol, DMSO, DMF, butanol and pyridine. The solubility of insoluble / sparingly soluble polymers at room temperature were tested at higher temperature. The grafted polymers were completely soluble in water, ethanol and pyridine, but insoluble in DMF.

2.2 Characterization techniques

2.2.1 FT-IR spectrometer

FT-IR spectra of monomer and polymers were recorded using Bruker Tensor -27 Spectrometer in the range of 400 cm^{-1} – 4000 cm^{-1}.

2.2.2 X-Ray diffraction

The X- RAY diffraction pattern of the synthesized polymers was recorded in a Pan – analytical X –RAY diffractometer.

2.2.3 UV-VIS spectroscopy

UV – visible absorption spectra of dry PEG-g-A were recorded using systronics – PC based double beam spectrometer 2202. The absorption was recorded in the range of 200-600 nm.

2.3 Corrosion inhibition studies

Corrosion monitoring techniques like potentiodynamic Polarization (Tafel polarization) and Electrochemical impedance spectroscopy (EIS) have been carried out using Solartron electrochemical measurement unit (1284 Z) model with a software package of Z plot and Corrware. The potentiodynamic polarization studies were carried out over a potential range of –200 mV to + 1500 mV with respect to reference electrode (calomel), counter electrode (platinum) and mild steel as working electrode, and current response was measured at a scan rate of 1 mV/sec. AC amplitude of 10 mV was applied and frequency varied from 10 KHz – 10 MHz. The real and imaginary parts of the impedance were plotted as Nyquist plot.

2.3.1 Measurement of Corrosion Current (I_{corr})

Values of corrosion currents were obtained by Tafel extrapolation method. In Tafel extrapolation method, plots of η Vs log I were made and an extrapolation of linear portion to the corrosion potential gave the corrosion current and the slope of the linear portion of the anodic and cathodic curves gave ba and bc respectively.

2.3.2 Determination of inhibition Efficiency

The inhibition Efficiency was obtained from all the parameter measured namely I_{corr}, R_p, R_{ct} and surface coverage were calculated using following equation. I_{corr}, R_p, R_{ct} are parameters calculated for inhibited solutions, and I^o_{corr}, R^o_p, R^o_{ct} are parameters obtained for uninhibited acid solution.

$$IE(\%) = \frac{Rct - Rct^{\circ}}{Rct};\ \frac{Rp - Rp^{\circ}}{Rp};\ \frac{I^{\circ}corr - Icorr}{I^{\circ}corr}$$

3. RESULTS & DISCUSSION

3.1Fourier Transform Spectrum-PEG-g-A

Fig.1 shows the infrared spectrum of the synthesized polymer PEG-g-A. The infrared spectra shows characteristic peaks at 1124 cm^{-1} due to the characteristic C-O-C stretching vibrations of the repeated $–OCH_2CH_2$ group of the polyethylene glycol (Zhao *et al.* *2010*), and the peak at 1317 $cm^{-1}$is due to the presence of hydroxyl groups in polyethylene glycol. The peak at 1635 cm^{-1} is due to the C=O stretching vibration. The presence of peak at 766 cm^{-1} shows rocking vibration of COO^{-} group. The absence of peaks due to NH_2 groups confirms the amide linkage in the grafted polymer. The absence of fundamental vibration of –CH bending near 2900-3500 cm^{-1} indicate the grafting of the amino acid on the poly ethylene glycol chain.

3.2 X-ray diffraction

The X-ray powder diffraction patterns of the prepared mixtures of PEG and arginine-grafted PEG are depicted in fig. 2 (Ravindran *et al.* 2012) and fig. 3 respectively. The classic approach based on one peak can be applied instead of the Rieteveld method. Fitting the whole diffraction pattern to the calculating intensity for the various phases that are present can give more precise results. The XRD patterns of PEG appears at 2? =19.2 °& 23.4 °. The XRD patterns of the grafted polymer contains the peaks in the range of 2?=18 °-28 ° and several new peaks in the range of 2?=30 °-40 °. Fig.2 shows shift in the peaks of PEG and appearance of several new peaks of polyarginine, which is a proof for the formation of grafted polymer. However, the sharp peaks of the grafted PEG reveal the crystalline nature of the polymer.

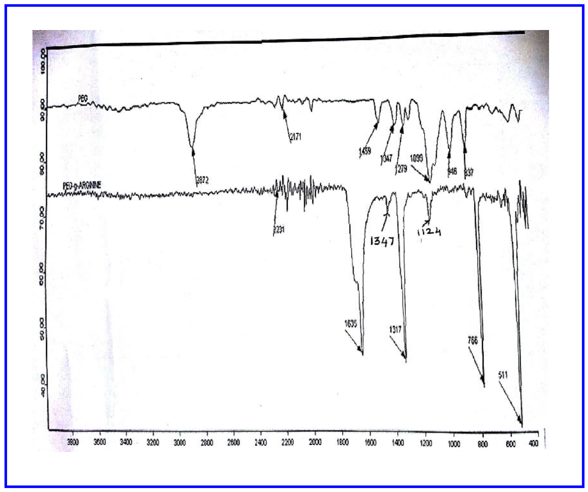

Fig. 1: FTIR Spectrum of PEG-g-A

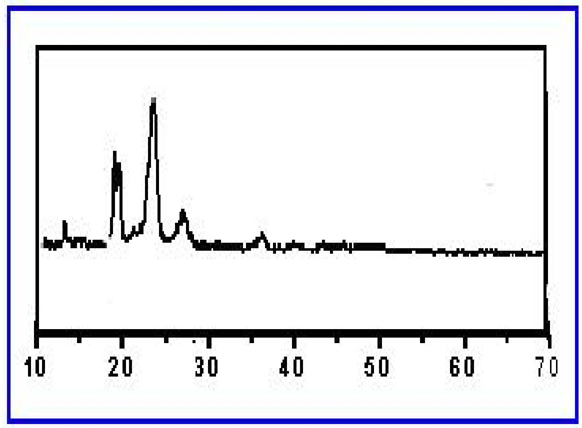

Fig. 2: X-ray Diffractogram of PEG

3.3 UV visible spectroscopy

The spectra of PEG and PEG-g-A polymers are depicted in Fig. 4 & Fig. 5 respectively. The grafted polymer shows absorption peak around 230-240mµ, where PEG lack of chromophores and auxochromes hardly shows any absorption. There is a slight shift, compared to the pure arginine (λ max at 206 mµ as reported by Saidel *et.al*. (1952)). The shift may be due to the formation of polyamides during polymerization.

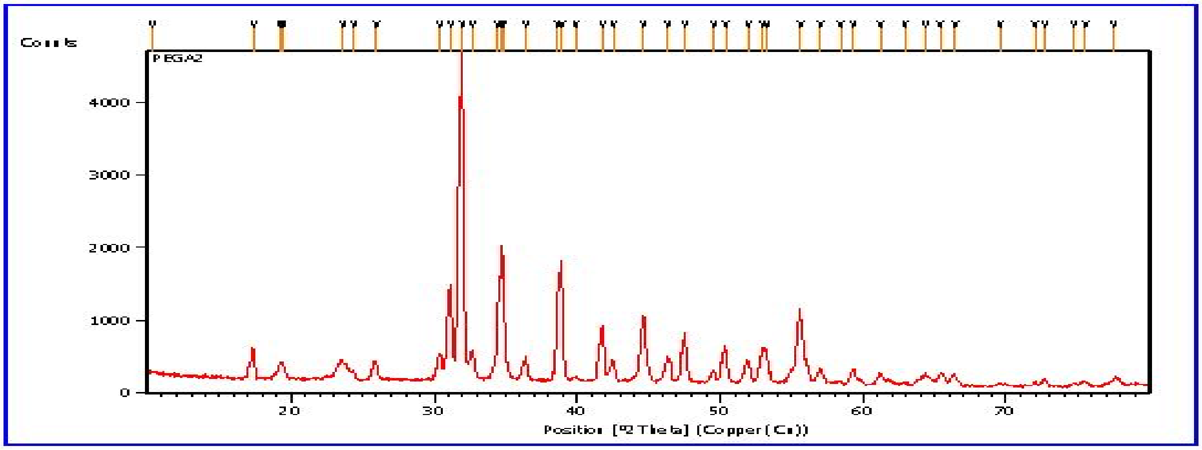

Fig. 3: X-ray Diffractogram of PEG-g-A

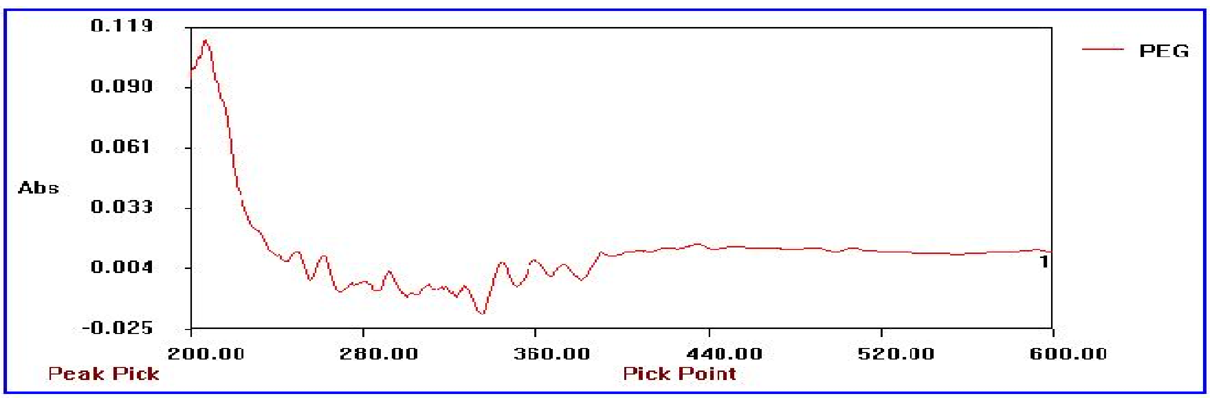

Fig. 4: UVAbsorption spectrum of PEG

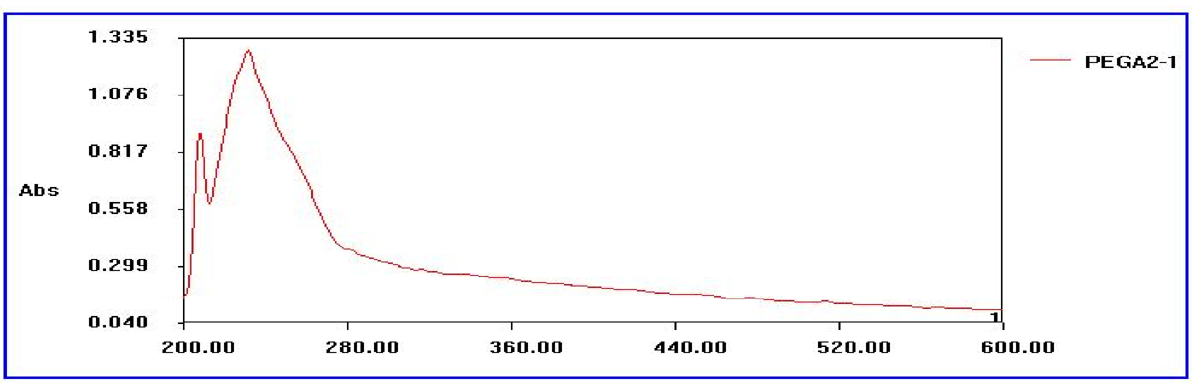

Fig. 5: UV-Absorption spectrum of PEG- F

3.3 UV visible spectroscopy

The spectra of PEG and PEG-g-A polymers are depicted in Fig. 4 & Fig. 5 respectively. The grafted polymer shows absorption peak around 230-240mμ, where PEG lack of chromophores and auxochromes hardly shows any absorption. There is a slight shift, compared to the pure arginine (λmax at 206mμ as reported by Saidel *et al.* 1952). The shift may be due to the formation of polyamides during polymerization.

4. ELECTROCHEMICAL MONITORING OF THE CORROSION INHIBITION BEHAVIOUR OF PEG-g-A FOR MILD STEEL IN ACID MEDIA

4.1 Potentiodynamic Polarization measurements

Polarization curves for mild steel in presence and absence of PEG-g-A in 1N HCl and 0.5M H_2SO_4 are shown in fig. 6. The extrapolation of Tafel straight line allows the calculation of the corrosion current density (I_{corr}). The values of I_{corr}, E_{corr}, Tafel slopes (b_a, b_c) and inhibition efficiency are given in table 1. The change in b_a and b_c values indicates the adsorption of PEG-g-A and modification of the mechanism of anodic dissolution as well as cathodic hydrogen evolution. The values of I_{corr} decreased in the presence of the grafted polymer which indicates the decrease in the rate of electrochemical reaction due to the formation of barrier layer on the mild steel surface (Sabirneeza *et al.* 2003). The increase in R_p values with the addition of inhibitor infers the retardation of mild steel corrosion. It is clear that there is no definite shift of E_{corr} values in the presence of inhibitor PEG-g-A. From all these inferences, PEG-g-A can be classified as mixed type inhibitor in both the acid mediums. But the inhibition efficiency calculated from the I_{corr} values and Rp values show that the polymer is an effective inhibitor in the sulphuric acid than hydrochloric acid.

4.2 AC Impedance measurements

The impedance behavior of MS in the presence of uninhibited and inhibited solutions is shown in the fig. 7. The curves in the Nyquist plot are depressed in nature with its centre below the x-axis. TF is observation is due to the micro roughness and other inhomogeneity at the solid electrode-solution interface formed during corrosion. The impedance parameters such as charge-transfer resistance (Rct) and double layer capacitance (Cdl) are obtained from the curves and are given in table 2. In the presence of the inhibitor in both the acid solutions, the Rct values increased and the Cdl values decreased. The increase in the Rct values are attributed to the adsorption of the polymer under investigation on the mild steel surface by replacing the water molecules at the metal-solution interface (Ravindran *et al.* 2012 and Quraishi *et al.* 2003). Decrease in Cdl is due to a decrease in the thickness of the electrical double layer. This indicates that the inhibitor adsorb at the metal solution interface.

4.3 Open Circuit potential

Fig. 8 shows the variation in open circuit potential of mild steel in 1N HCl and H_2SO_4 in presence PEG-g-A at room temperature as a function of exposure time. The potentials drift to the positive direction with time in the presence of polymers compared to the pure acid. This is associated with the formation of inhibiting of oxide film. The system tends to stabilize at an average value for long exposure time.

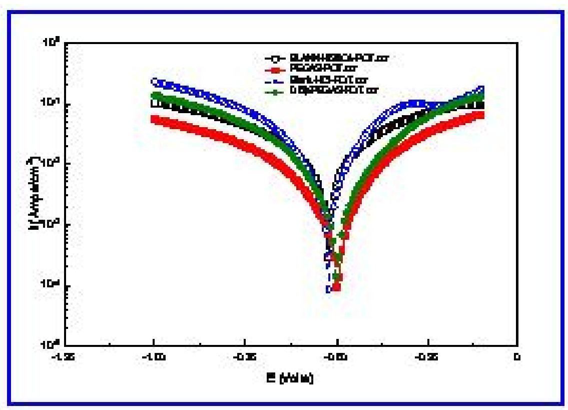

Fig. 6: Potentiodynamic polarization curves for mild steel in the prescence and absence of PEG-g-A

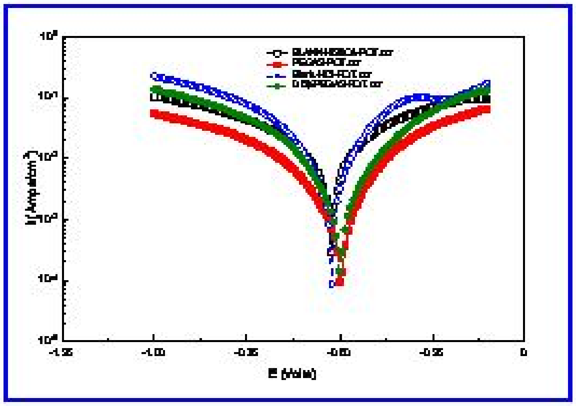

Fig. 7: Nyquist Plot for mild steel in the presence and absence of PEG-g-A

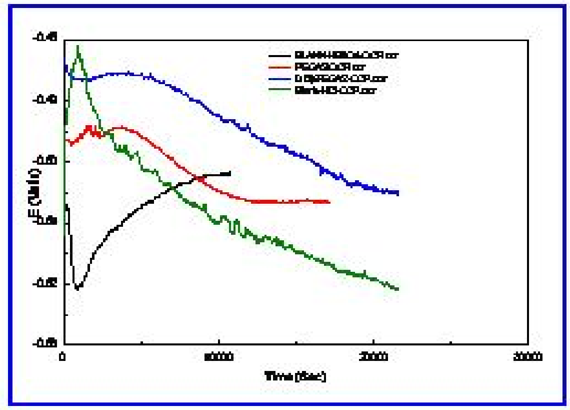

Fig. 8: Open circuit potential plot of MS in the presence and absence of PEG-g-A

Table 1. Electrochemical parameters of PEG-g-Arginine for Mild steel in HCl and H_2SO_4

S.No.		BA(MV)	BC(MV)	E_{CORR} (MV)	ICORR ? A/CM^2	IE (%)	RP OHMS	IE (%)
1	BLANK HCL	128.62	106.73	-520	293.02	---	8.2	----
2	HCL+PEG-G-A	102	90	-490	68.432	77	18.3	55
3	BLANK H_2SO_4	274.13	201.6	-520	777.4	---	5.7	----
4	H_2SO_4+PEG-G-A	120.84	96.534	-497	48.18	94	32	77

Table 2. Impedance parameters of PEG-g-Arginine for Mild steel in HCl and H_2SO_4

S.No.		Cdl (F)*10^{-5}	IE(%)	Rct(ohms)	IE (%)
1	BLANK HCL	22.14	-----	58.44	----
2	HCL+PEG-G-A	7.329	63.6	137.26	57.42
3	BLANK H_2SO_4	15.39	-----	10.612	----
4	H_2SO_4+PEG-G-A	6.897	65.5	68.34	94.23

5. CONCLUSION

A graft polymer of PEG-g-arginine in three different ratios was synthesized by free radical polymerization. The corrosion inhibition behavior of the synthesized polymer was monitored electrochemically, which revealed the corrosion inhibition potential of the polymer. The polymer showed a good corrosion inhibition performance in the sulphuric acid medium than hydrochloric acid medium.

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